14 COPPER AND ZINC

Copper, like Fe, participates in oxidation-reduction processes in plants. Copper is associated with enzymes that can hydroxylate monophenols, oxidizing them to create complex polymers such as lignin and melanin; detoxify superoxides; oxidize amines; terminate electron transfer chains; and act generally as cytoplasmic oxidases (Tisdale et al., 1985).

Newly reclaimed acid histosols (organic soils) are invariably Cu deficient, hence the name reclamation disease. In the United States Cu deficiency is most common in Florida, Wisconsin, Michigan, and New York, where vegetable and fruit crops are grown. Similarly, in Canada the Cu deficiency has been reported from Manitoba, Alberta, Saskatchewan, and Prince Edward Island. Responses of cereals to Cu have been reported from Australia (Robson et al., 1984), the United States (Varvel, 1983), Scotland (Reith, 1968), and Canada (Karamanos et al., 1986).

Zinc is a transition element, but has no impaired electrons; both the third and fourth orbitals are filled. Zinc ion (Zn^{2+}) is formed by the loss of the 4S electrons, and reactions tend to be similar to those of Ca^{2+} (Harter, 1991). Zinc is involved in a diversity of enzymatic activities such as auxin metabolism, dehydrogenases, phosphodiesterase, and the promotion of synthesis of cytochrome C. Zinc deficiencies are more prevalent than those of Cu and are virtually global in nature. In the United States and India most states now recognize the need for supplemental Zn for one or more crops. Analysis of about 40,000 soil samples from different parts of India showed 50% of the samples to be deficient in plant available Zn (Katyal and Sharma, 1979). Large areas of Zn deficiency have been identified in Canada, Europe, Great Britain, Australia, New Zealand, Central and South Africa, and Brazil. Acidic, sandy soils low in total Zn, calcareous soils, soils heavily fertilized with phosphorus, and subsoils exposed by land leveling operations or by wind and/or water erosion are prone to zinc deficiency.

While the chemistry in soils and the functions in plants of Cu and Zn differ greatly, there are several similarities:

1. Both are metals.
2. Both are taken up by plants as cations in +2 valence, as Cu^{2+} and Zn^{2+}.

3. Both Cu and Zn have a strong tendency to combine with S and occur as sulfides in the lithosphere.
4. Both Cu and Zn have three ionic forms in soil solution with possible valencies of +2, +1, and 0.

14.1. AMOUNTS IN SOIL

The Cu content in soils ranges from nearly 5 to 60 mg kg^{-1}, although both lower (<2 mg kg^{-1}) and higher values are not uncommon (Stevenson, 1986). The average value of Cu in soils is about 9 to 10 mg kg^{-1}. The most widely occurring copper mineral is chalcopyrite ($CuFeS_2$). Other Cu-bearing minerals are chalcocite (Cu_2S) and bornite ($CuFeS_4$).

Total Zn content in soils ranges from 10 to 300 mg kg^{-1} with an average of 50 mg kg^{-1}. The Zn content in various rocks varies from 4 to 100 mg kg^{-1}. The general values (mg kg^{-1}) are basalt 100, shale 45, granite 10, limestone 4, and sandstone 30 mg kg^{-1} (Tisdale et al., 1985; Stevenson, 1986). The most important minerals are sphalerite (ZnS), smithsonite ($ZnCO_3$), and hemimorphite ($Zn_4(OH)_2Si_2O_7.H_2O$).

14.2. FORMS OF COPPER AND ZINC IN SOILS

Both Cu and Zn occur in soils in the following forms:

1. As a structural component of clay minerals. Zinc can substitute for Mg in the crystal lattice. A large part of the Zn present in soil exists as a component of augite, hornblende, and biotite, which are known as ferromagnesium minerals.
2. Adsorbed on clay mineral surfaces—partly as exchangeable cations.
3. Adsorbed on the oxides, hydroxides, and oxyhydroxides of Fe and Al. Some of the Cu so adsorbed may be occluded by oxide minerals because Cu readily coprecipitates with Fe and Al. Zinc is also adsorbed on carbonates.
4. Complexed with soil organic matter.
5. Present as Cu^{2+} and Zn^{2+} in soil solution.

Different forms of Cu or Zn tend to maintain an equilibrium in soil.

14.2.1. Copper and Zinc in Soil Solution

The concentrations of both Cu^{2+} and Zn^{2+} in soil solution remain very low, approximately 0.5 to 70 mg Mg^{-1} (ppb). At any time the concentration of Zn^{2+} in the soil solution is generally greater than that of Cu^{2+}. Plant uptake of Cu^{2+} is mostly by root interception, while that of Zn^{2+} is by diffusion.

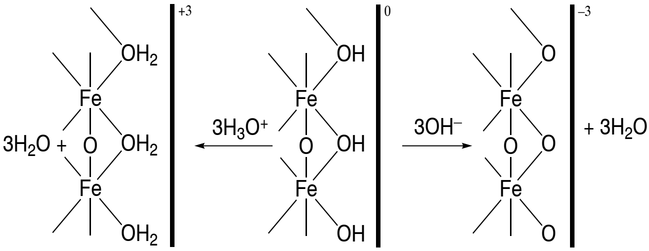
Both Cu and Zn are present in three ionic forms—M^{2+}, $M(OH)^+$, and $M(OH)_2^0$, where M stands for Cu and Zn. At pH <6.0 nearly all Cu and Zn are present as Cu^{2+} or Zn^{2+}. As pH approaches neutrality, nearly half the Cu in soil solution is hydrolyzed to $Cu(OH)_2^0$, and the change to this form is 92% at pH 8. This change in form reduces Cu availability to plants. In contrast $Zn(OH)_2^0$ begins to appear only at pH 8. Reduction in the divalent form of Zn^{2+} to the hydrolyzed form is slower for Zn. At pH 7 about 83% is still present as Zn^{2+} and 31% at pH 8. At pH 8 about two-thirds of Zn may be present as $Zn(OH)^+$, which is less available to plants.

14.2.2. Copper and Zinc Adsorbed onto Clay Minerals

Copper can be sorbed by clay minerals at lower activities than those required for Zn. Thus it is suggested that Cu^{2+} is retained by specific sorption sites, while Zn^{2+} is retained on nonspecific sites. Although quite divergent data are available, 2:1 layer silicates in general adsorb more Cu^{2+} and Zn^{2+} than 1:1 layer silicates (Farrah, et al., 1980); Krishnasamy et al., 1985).

14.2.3. Copper and Zinc Adsorbed onto Fe and Al Hydrous Oxides

Hydrous oxides of Fe and Al play an important role in the retention of Cu and Zn and their concentration in soil solution. Removal of hydrous oxides of Fe and Al can significantly reduce the Cu^{2+} and Zn^{2+} retention capacity of soil (Cavallrao and McBride, 1984). Also since Fe and Al oxides have a variable charge, retention of Cu^{2+} and Zn^{2+} by these oxides depends very much upon soil pH. Zn^{2+} may be adsorbed by oxides specifically (irreversibly) or nonspecifically. The specific or irreverisble sorption mechanism proposed by Quirk and Posner (1975) is shown below:



14.2.4. Copper and Zinc Adsorbed by Organic Matter

Soil organic matter also plays an important role in the retention of both Cu and Zn, more so for Cu than for Zn. Carboxylate and phenolic group and N lone-pair electrons are the dominant retention sites for Cu^{2+} (Harter, 1991).

Table 14.1 Effect of pH on Solution Composition of Cu and Zn, Expressed as Percent in Solution

pH	4	5	6	7	8
Cu^{2+}	100	100	96	33	1
$CuOH^{+}$			2	7	1
$Cu(OH)_2^0$			2	56	92
Zn^{2+}	100	100	98	83	31
$ZnOH^{+}$			2	17	64
$Zn(OH)_2^0$					5

From Harter, 1983. Soil Sci. Soc. Am. J. 47:49. With permission of SSSA.

14.3. FACTORS AFFECTING THE AVAILABILITY OF COPPER AND ZINC

The availability of Cu and Zn to plants is affected by a number of factors such as pH, kind and amount of organic matter, interaction with other elements in soil solution, fertilizer practices, soil amendments, flooding (as in rice culture), environmental factors, and plant factors.

14.3.1. Soil pH

The influence of soil pH on the solubility and ionic species of Cu and Zn in soils has already been discussed. In general, increases in soil pH above 6.0 decreases the availability of Cu and Zn due to the following:

1. A change in the hydrolysis status—for example, at pH 8 Cu $(OH)_2^0$ and Zn $(OH)^{+1}$ are the dominant ionic species (Table 14.1), which have less solubility (activity) than Cu^{2+} and Zn^{2+}.
2. Increased sorption on Al and Fe oxides and hydroxides, clay minerals, and soil organic matter due to increased pH-dependent charge.
3. Reduced competition with H^+ for the adsorption sites.
4. A change in the quantity and nature of organic binding chemicals; for example, zinc complexing by humic acids increases with rising pH.

14.3.2. Interaction With Other Elements in Soil

High concentrations of Zn, Al, P, and Fe in soil solution restrict Cu absorption by plants. Similarly, Cu, Fe, and Mn inhibit uptake of Zn (Kausar, et al., 1976; Giordano et al., 1974). This is possibly due to competition for the carrier sites on roots.

The most frequently reported and researched interaction is P x Zn, namely, phosphorus-induced Zn deficiency. Application of high rates of P enhances the adsorption of Zn in some soils, especially those rich in Fe and Al oxides and hydroxides (Saeed and Fox, 1979). This could be due to the additional negative charge or complexation sites created due to sorption of PO_4^{3-} into oxide surfaces (Bolland et al., 1977). Furthermore, physiological research has brought out that high P rates increase the amount of Zn in the ethanol-soluble and pectate fraction of root cell walls, and this binding of Zn results in reduced amounts of Zn available for transport to the plant shoot (Youngdahl et al., 1977). An alternative hypothesis suggests that what is generally considered a Zn deficiency is in reality P-toxicity due to higher uptake of P (Webb and Loneragan, 1988). Whatever the explanation, large amounts of data (Adams, 1980) suggest the presence of a negative P × Zn interaction under field conditions.

14.3.3. Fertilizer Practices

Application of high rates of NPK fertilizers has aggravated Cu and Zn deficiencies. In addition to P × Zn interaction effects, a number of other factors listed below are responsible for this:

1. Increased fertilization results in increased yields and thus increased demands for Cu and Zn (this would apply for other nutrients as well).
2. Increased fertilization results in greater depletion of Cu and Zn (also other plant nutrients) from soils and thus increases the chances of their deficiencies occurring.
3. Addition of large amounts of N-fertilizers can increase soil acidity, which may increase Al and Fe levels in soils and thereby depress the absorption of Cu and Zn by plant roots.

14.3.4. Soil Amendments

The application of lime ($CaCO_3$) to acidic soils and gypsum ($CaSO_4.5H_2O$) on sodic soils affects the availability of these nutrients. When lime is added to acidic soils, or in calcareous soils where free $CaCO_3$ is present, zinc can be adsorbed on $CaCO_3$ particles, which may temporarily reduce Zn availability. In the long run, however, $ZnCO_3$ becomes available to plants because its solubility is too high to persist in soils.

The application of gypsum on sodic soils increases the availability of Zn (1) because of slight lowering of pH and (2) because the highly mobile $ZnSO_4^0$ (an important species of Zn in soils) contributes significantly to soil solution Zn.

14.3.5. Flooding or Submergence

Flooding or submergence of fields, as practiced in paddy rice culture results in increased pH on acidic soils and therefore is likely to reduce Zn availability (Mikkelsen and Brandon, 1975). The reverse could be true on alkaline or sodic soils. The formation of ZnS under the anaerobic conditions created is also responsible for decreased Zn availability (Ponnamperuma, 1972).

14.3.6. Weather Conditions

In cooler regions the availability of Cu and Zn increases with an increase in temperature (Moraghan and Mascagnie, 1991). The severity of Zn deficiency increases under reduced or intermediate light (Edwards and Kamprath, 1974). Thus Zn deficiency symptoms appear when days are cool and cloudy.

14.3.7. Plant Factors

There are genotypic differences in plant species in respect of sensitivity to Cu or Zn deficiency. Among small grains, rye has exceptional tolerance to Cu deficiency. The usual order of sensitivity of the small grains to Cu deficiency in the field is wheat > barley > oats and rye (Tisdale et al., 1985). The sensitivity of different crops to Cu and Zn are given in Tables 14.2 and 14.3.

14.4. SOIL TESTS FOR COPPER AND ZINC

14.4.1. Copper

Two extractants tested and used for upland crops are 0.05 *M* EDTA (pH 7.0) (Reith, 1968) and Mehlich-Bowling (0.5 *M* HCl + 0.016 *M* $AlCl_3$) (Makarin and Cox, 1983). The critical value for barley and oat for the 0.05 *M* EDTA extractable Cu is 1.1 mg kg^{-1}, while that for soybean and wheat using Mehlich-Bowling extract is 0.7 mg Cu kg^{-1} soil.

14.4.2. Zinc

There are four extractants generally used for determining available Zn in soils, namely, 0.1 *M* HCl (Wear and Sommer, 1948), EDTA-$(NH_4)_2CO_3$ (Trierweiler and Lindsay, 1969), Dithizone—NH_4OAC (Tierweiler and Lindsay, 1969), and DTPA-TEA (Brown et al., 1971). The first proposed extractant was 0.1 *M* HCl, and it is now used the least. Dithizone—NH_4OAC extraction of zinc involves the use of CCl_4, which is hazardous to human health and is therefore less adaptable to routine use, yet this method has been widely used. Dithizone—NH_4OAC and DTPA-TEA were equally

Table 14.2 Relative Sensitivity of Crops to Cu Deficiency

Low	Medium	High
Barley	Broccoli	Alfalfa
Beans	Cabbage	Cauliflower
Blueberry	Carrot	Celery
Cucumber	Clover	Sugarbeet
Corn	Lettuce	Turnip
Sudan Grass	Radish	
Oat	Spinach	
Onion	Sweet corn	
Pea	Tomato	
Potato		
Rye		
Sorghum		
Soybean		
Wheat		

From Martens and Westermann. 1991. *Micronutrients in Agriculture*, 2nd ed., J.J. Mortvedt, F.R. Cox, L.M. Shuman, and R.M. Welch, Eds. With permission of SSSA.

Table 14.3 Sensitivity of Crops to Low Levels of Available Zinc in Soils

Sensitive	Moderately tolerant	Tolerant
Corn	Grain sorghum	Alfalfa
	Clover	Barley
Field beans	Potatoes	
	Forage	Oats
	Sorghum	Millet
Sweet corn	Soybeans	Rye
	Sugar beets	Wheat
Rice[a]	Sudan grass	Grasses

[a] Added by authors.

From Rehm and Penas, 1982. NebGuide, G82-596. With permission of the University of Nebraska, Lincoln.

effective in the separation of 92 California soils into Zn-sufficient and Zn-deficient groups for sweet corn production (Brown et al., 1971). The critical values for DTPA-TEA are from 0.5 to 0.8 mg Zn kg^{-1} soil for corn (Brown et al., 1971; Lindsay and Norvell, 1978), 0.48 mg Zn kg^{-1} soil for green gram (Gupta and Mittal, 1981), and 0.86 mg Zn kg^{-1} soil for rice (Singh and Takkar, 1981).

14.5. DEFICIENCY SYMPTOMS IN PLANTS

14.5.1. Copper

In cereals such as wheat and oats receiving adequate Cu supply the Cu concentration at boot stage may vary from 5 to 21 mg kg^{-1}, while in forage alfalfa and timothy (*Phleum pratense* L.) it may vary from 9 to 54 mg kg^{-1} dry matter (Gupta, 1989a). Deficiencies are likely when Cu concentration in plant dry matter falls below 4 mg kg^{-1} (Tisdale et al., 1985). On the other hand, Cu concentration as high as 55 mg kg^{-1} in timothy and wheat exhibited no toxicity.

Symptoms of Cu deficiency appear first at the top of the plant with the youngest leaves becoming yellow and pale as the deficiency advances. Eventually, dead tissue appears along the tips and edges of leaves as in the case of K. In vegetables the leaves lack turgor and develop a bluish green cast (Tisdale et al., 1985). Copper deficiency symptoms in barley and wheat are shown in Figure 14.1. Crops most susceptible to Cu deficiency are alfalfa, wheat, barley, oats, and onions.

14.5.2. Zinc

In cereals such as wheat and barley receiving adequate Zn supply, plant concentrations at boot stage may vary from 20 to 123 mg kg^{-1} dry matter (Gupta, 1989b) or even higher. Zinc deficiency in plants may be expected when the plant concentration is less than 20 mg kg^{-1} dry matter, while Zn toxicity can occur when concentrations exceed 400 mg kg^{-1} dry matter (Tisdale et al., 1985).

Corn and beans in field crops and citrus in orchard crops are sensitive to zinc deficiency. Experience in Asian countries has shown that rice is also sensitive to Zn deficiency.

Since Zn is highly immobile in plants, its deficiency symptoms are seen on the growing points and young leaves. In corn the young leaves become yellow to white (sometimes stripped) and the plant has stunted growth; therefore the name “white bud” (Figure 14.2). Zinc deficiency in rice fields is indicated by areas of chocolate-brown, burned-up plants, hence the name “Khaira” disease. In citrus the deficiency is indicated by a cluster of leaves (rosette) at the top of mainly bare branches, referred to as “mottle leaf” or “frenching.” Some other zinc deficiency diseases are “little leaf” in cotton and “fern leaf” in russet Burbank potatoes.

Crops sensitive, tolerant, and moderately tolerant to zinc deficiency are listed in Table 14.3.

14.6. COPPER AND ZINC FERTILIZERS

A list of Cu and Zn fertilizers is given in Table 14.4. The most popular and widely used source of Cu is $CuSO_4.5H_2O$ and that of Zn is $ZnSO_4$. Generally, a dose of 10 to 25 kg ha^{-1} $CuSO_4$ or $ZnSO_4$ is recommended on Cu/Zn deficient soils, depending upon soil texture; the heavier the texture, the

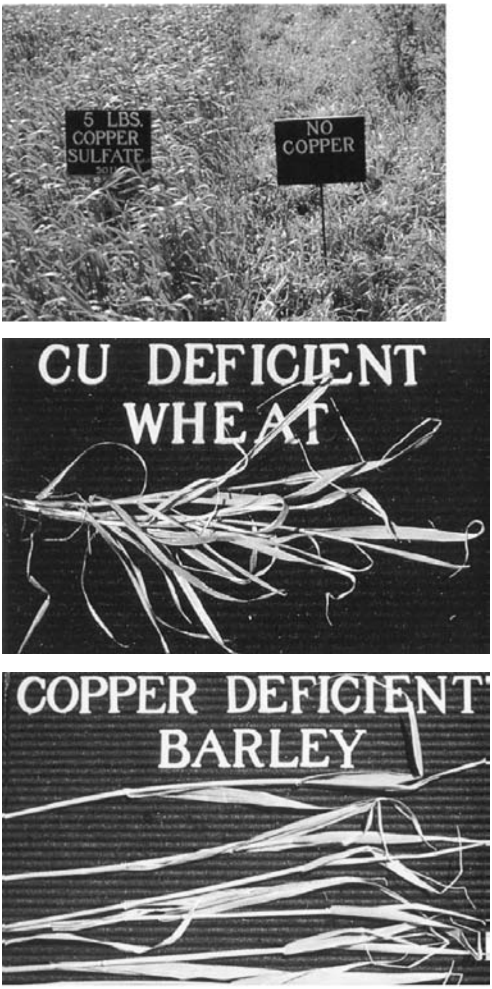


Figure 14.1. Copper deficiency in wheat (above) and barley. (From *Small Grains Field Manual*, pp. 11–12, J.R. Simplot Co. Minerals & Chemical Division, Pocatello, ID, ©1984. With permission.) See Plate 8 following p. 170.

greater the dose. In general, soil application of Cu, as well as Zn, is considered more effective. When a deficiency is observed in a standing crop, foliar applications can also be made. A 0.5% w/v solution of $CuSO_4$ or $ZnSO_4$ is recommended with a small amount of slaked lime (0.5 kg 100 l^{-1}); this practice prevents scorching of leaves. Dosages are much less when chelates are used, and these are preferably used for foliar application. Dipping of rice seedlings or cut potato-seed pieces in a 2%-$ZnSO_4$ or -ZnO suspension or slurry is an economical way of applying Zn to crops on Zn-deficient soils; only 2 to 5 kg ha^{-1} $ZnSO_4$ or ZnO are required with this method.

Figure 14.2. **Zinc deficiency in maize (corn). (From *Corn Field Manual*, pp. 9–10, J.R. Simplot Co. Minerals & Chemical Division, Pocatello ID, ©1984. With permission.) See Plate 9 following p. 170.**

Table 14.4 Copper and Zinc Fertilizers

Source	Formula	Cu or Zn (%)
Copper		
Copper sulfate monohydrate	$CuSO_4.H_2O$	35
Basic copper sulfates	$CuSO_4.3Cu(OH)_2$	13–53
Copper ammonium phosphate	$Cu(NH_4)PO_4.H_2O$	32
Copper chelates	$Na_2CUEDTA$	13
	NaCuHEDTA	9
Copper-sulfur frits		0.5–20
Zinc		
Zinc sulfate monohydrate	$ZnSO_4.H_2O$	35
Zinc sulfate heptahydrate	$ZnSO_4.H_2O$	23
Basic zinc sulfate	$ZnSO_4.6Zn(OH)_2$	55
Zinc oxide	Zno	78
Zinc phosphate	$Zn_3(PO_4)_2$	51
Zinc chelates	$Na_2ZnEDTA$	14
	NaZnNTA	13
	NaZnHEDTA	9
Zinc frits		Variable

From Murphy and Walsh, 1972. *Micronutrients in Agriculture*, J.J. Mortvedt, P.M. Giordano, and W.L. Lindsay, Eds., p. 351. With permission of SSSA.

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